Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

One-dimensional polymeric polybromotellurates (IV): structural and theoretical insights

Andrey N. Usoltsev,[a] Sergey A. Adonin,[*a,b] Alexander S. Novikov,[c] Denis G. Samsonenko,[a,b] Maxim N. Sokolov[a,b] and Vladimir P. Fedin[a,b]

Table 1S. Selected bond lengths and angles for **1**.

Bond	*d*, Å	Bond	*d*, Å
Te(1)–Br(1)	2.6054(4)	Te(1)–Br(3)	2.8209(4)
Te(1)–Br(2)	2.6939(3)	Br(4)–Br(4)^{i}	2.3383(6)
Angle	ω, deg.	Angle	ω, deg.
Br(1)–Te(1)–Br(1)^{ii}	90.650(16)	Br(1)–Te(1)–Br(3)	177.455(11)
Br(1)^{ii}–Te(1)–Br(2)^{ii}	90.569(10)	Br(2)–Te(1)–Br(2)^{ii}	175.618(18)
Br(1)–Te(1)–Br(2)	90.571(10)	Br(2)–Te(1)–Br(3)	87.891(10)
Br(1)–Te(1)–Br(2)^{ii}	92.510(10)	Br(2)–Te(1)–Br(3)^{ii}	88.917(10)
Br(1)–Te(1)–Br(3)^{ii}	91.442(10)	Br(3)–Te(1)–Br(3)^{ii}	86.503(15)

Symmetry transformations used to generate equivalent atoms:

i) $-x + 3/2, -y + 3/2, -z + 1$; ii) $-x + 1, y, -z + ½$.

Table 2S. Selected bond lengths and angles for **2**.

Bond	*d*, Å	Bond	*d*, Å
Te(1)–Br(11)	2.8192(4)	Te(2)–Br(23)	2.9439(5)
Te(1)–Br(12)	2.6608(4)	Te(2)–Br(24)	2.6637(4)
Te(1)–Br(13)	2.5999(4)	Te(2)–Br(25)	2.6880(4)
Te(1)–Br(14)	2.5681(5)	Te(2)–Br(26)	2.7165(4)

Te(1)–Br(15)	2.7123(4)	Br(1)–Br(1)[i]	2.3396(8)
Te(1)–Br(16)	2.8887(5)	Br(2)–Br(2)[ii]	2.3300(8)
Te(2)–Br(21)	2.5632(4)	Br(3)–Br(4)	2.3289(6)
Te(2)–Br(22)	2.6820(4)		

Angle	ω, deg.	Angle	ω, deg.
Br(11)–Te(1)–Br(16)	87.024(13)	Br(21)–Te(2)–Br(22)	91.144(14)
Br(12)–Te(1)–Br(11)	91.635(14)	Br(21)–Te(2)–Br(23)	177.639(15)
Br(12)–Te(1)–Br(15)	177.989(15)	Br(21)–Te(2)–Br(24)	89.692(14)
Br(12)–Te(1)–Br(16)	88.325(14)	Br(21)–Te(2)–Br(25)	90.942(14)
Br(13)–Te(1)–Br(11)	179.206(16)	Br(21)–Te(2)–Br(26)	90.719(14)
Br(13)–Te(1)–Br(12)	88.802(14)	Br(22)–Te(2)–Br(23)	91.109(13)
Br(13)–Te(1)–Br(15)	89.737(14)	Br(22)–Te(2)–Br(25)	177.542(15)
Br(13)–Te(1)–Br(16)	92.327(14)	Br(22)–Te(2)–Br(26)	92.303(13)
Br(14)–Te(1)–Br(11)	88.474(14)	Br(24)–Te(2)–Br(22)	89.232(13)
Br(14)–Te(1)–Br(12)	90.457(15)	Br(24)–Te(2)–Br(23)	91.046(13)
Br(14)–Te(1)–Br(13)	92.185(15)	Br(24)–Te(2)–Br(25)	89.478(13)
Br(14)–Te(1)–Br(15)	90.980(15)	Br(24)–Te(2)–Br(26)	178.402(15)
Br(14)–Te(1)–Br(16)	175.300(15)	Br(25)–Te(2)–Br(23)	86.823(13)
Br(15)–Te(1)–Br(11)	89.809(13)	Br(25)–Te(2)–Br(26)	88.971(14)
Br(15)–Te(1)–Br(16)	90.353(14)	Br(26)–Te(2)–Br(23)	88.484(14)

Symmetry transformations used to generate equivalent atoms:

i) $-x, -y, -z$; ii) $-x + 1, -y + 1, -z$.

Table 3S. Selected bond lengths and angles for **3**.

Bond	*d*, Å	Bond	*d*, Å
Te(1)–Br(1)	2.6432(7)	Te(1)–Br(4)	2.7061(4)
Te(1)–Br(2)	2.6919(4)	Br(5)–Br(5)^{i}	2.3290(9)
Te(1)–Br(3)	2.7284(7)		
Angle	ω, deg.	Angle	ω, deg.
Br(1)–Te(1)–Br(2)	90.921(13)	Br(2)–Te(1)–Br(4)	88.024(13)
Br(1)–Te(1)–Br(3)	180.00(2)	Br(2)–Te(1)–Br(4)^{ii}	91.991(13)
Br(1)–Te(1)–Br(4)	89.509(12)	Br(4)–Te(1)–Br(3)	90.491(12)
Br(2)–Te(1)–Br(2)^{ii}	178.16(3)	Br(4)^{ii}–Te(1)–Br(4)	179.02(2)
Br(2)–Te(1)–Br(3)	89.079(13)		

Symmetry transformations used to generate equivalent atoms:

i) $-y + 1, x - 1, -z + 1$; ii) $x, y, -z + 1$.

Table 4S. Selected bond lengths and angles for **4**.

Bond	*d*, Å	Bond	*d*, Å
Te(1)–Br(1)	2.6944(4)	Br(4)–Br(4)^{i}	2.3199(8)
Te(1)–Br(2)	2.7006(3)	Br(5)–Br(6)	2.323(4)
Te(1)–Br(3)	2.6901(3)		
Angle	ω, deg.	Angle	ω, deg.
Br(1)^{ii}–Te(1)–Br(1)	180	Br(3)–Te(1)–Br(1)	90.165(10)
Br(1)–Te(1)–Br(2)	89.745(11)	Br(3)–Te(1)–Br(2)^{ii}	89.029(11)
Br(1)–Te(1)–Br(2)^{ii}	90.255(11)	Br(3)–Te(1)–Br(2)	90.971(11)

Br(2)^{ii}–Te(1)–Br(2)	180	Br(3)^{ii}–Te(1)–Br(3)	180
Br(3)–Te(1)–Br(1)^{ii}	89.835(10)		

Symmetry transformations used to generate equivalent atoms:

i) $-x + ½, y, -z + 1$; ii) $-x + ½, -y + ½, -z + ½$.

Table 5S. Selected bond lengths and angles for **5**.

Bond	*d*, Å	Bond	*d*, Å
Te(1)–Br(1)	2.6913(4)	Te(1)–Br(3)	2.7123(4)
Te(1)–Br(2)	2.6914(4)		
Angle	ω, deg.	Angle	ω, deg.
Br(1)–Te(1)–Br(1)^{i}	180	Br(1)–Te(1)–Br(3)^{i}	90.318(12)
Br(1)–Te(1)–Br(2)^{i}	89.700(13)	Br(2)^{i}–Te(1)–Br(2)	180
Br(1)–Te(1)–Br(2)	90.299(13)	Br(2)–Te(1)–Br(3)	91.690(13)
Br(1)–Te(1)–Br(3)	89.681(12)	Br(3)^{i}–Te(1)–Br(3)	180

Symmetry transformations used to generate equivalent atoms: i) $-x + 1, -y + 1, -z + 1$.

Computational details. The single point calculations based on the experimental X-ray geometries (quasi-solid-state approach) have been carried out at the DFT level of theory using the M06 functional [1] (this functional was specifically developed to describe weak dispersion forces and non-covalent interactions) with the help of Gaussian-09 [2] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using DZP-DKH basis sets [3-6] for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader [7] has been performed by using the Multiwfn program (version 3.3.8) [8]. The Cartesian atomic coordinates of model supramolecular clusters are presented in **Table 6S**.

[1] Y. Zhao et al., Theor. Chem. Acc. 2008, 120, 215

[2] M. J. Frisch et al., Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010

[3] C.L. Barros et al., Mol. Phys. 2010, 108, 1965

[4] A.C. Neto et al., Chem. Phys. Lett. 2013, 582, 158

[5] R.C. de Berredo et al., J. Mol. Struct. - Theochem 2010, 961, 107

[6] F.E. Jorge et al., J. Chem. Phys. 2009, 130, 064108

[7] R.F.W. Bader, Chem. Rev. 1991, 91, 893

[8] T. Lu et al., J. Comput. Chem. 2011, 33, 580

Table 6S. Cartesian atomic coordinates of model supramolecular clusters.

Atom	X	Y	Z
1			
Te	7.605790	1.824459	3.260374
Br	5.441945	1.927192	4.860565
Br	8.735715	3.879116	4.827961
Br	6.470018	-0.007610	1.797118
Br	9.769636	1.927192	1.660182
Br	6.475865	3.879116	1.692786
Br	8.741562	-0.007610	4.723629
Br	10.349309	6.254337	5.967788
Br	11.419952	8.014113	7.073707
Te	14.163471	12.443991	9.781121
Br	16.327316	12.341258	8.180929
Br	13.033546	10.389334	8.213533
Br	15.299243	14.276060	11.244376
Br	11.999625	12.341258	11.381312
Br	15.293396	10.389334	11.348708
Br	13.027699	14.276060	8.317865
2			
Te	11.639218	10.628602	4.189450
Br	13.300551	9.225287	2.618829
Br	12.055776	12.767404	2.656023
Br	9.910441	12.058385	5.670466
Br	11.153324	8.481650	5.782049
Br	9.327711	9.836520	2.549512
Br	13.586611	11.345728	5.694135
Te	7.329885	0.259084	12.725580
Br	7.849079	2.447398	11.026469
Br	9.412518	1.290469	14.441598
Br	6.857658	-1.738926	14.319870
Br	5.481806	1.739175	14.052746
Br	9.174646	-1.220761	11.508307
Br	5.555382	-0.532684	11.048448
Br	11.538291	2.802076	16.240457

Br	13.181500	3.805475	17.572695
Br	7.384829	8.104680	0.710076
Br	5.861576	7.059838	-0.710076
Br	9.108374	4.628351	9.227609
Br	9.925997	6.229955	7.746593
Te	17.389906	6.348467	21.087573
Br	16.870712	4.160154	22.786684
Br	15.307272	5.317083	19.371555
Br	17.862132	8.346477	19.493283
Br	19.237985	4.868377	19.760406
Br	15.545144	7.828313	22.304846
Br	19.164409	7.140236	22.764705
Te	1.607187	4.535916	-4.189450
Br	-0.054146	5.939231	-2.618829
Br	1.190628	2.397114	-2.656023
Br	3.335964	3.106133	-5.670466
Br	2.093080	6.682868	-5.782049
Br	3.918694	5.327998	-2.549512
Br	-0.340207	3.818789	-5.694135
3			
Te	3.404201	3.404201	12.884100
Br	5.332018	5.332018	12.884100
Br	5.179647	1.594684	13.829793
Br	2.831629	4.039235	15.437729
Br	1.534114	1.534114	12.884100
Br	1.594684	5.179647	11.938407
Br	4.039235	2.831629	10.330471
Br	-2.278931	8.787324	13.152089
Br	-0.676676	7.185069	12.616111
Te	-6.059799	12.868201	12.884100
Br	-4.131982	14.796018	12.884100
Br	-4.284353	11.058684	13.829793
Br	-6.632371	13.503235	15.437729
Br	-7.929886	10.998114	12.884100
Br	-7.869316	14.643647	11.938407
Br	-5.424765	12.295629	10.330471
6			
Br	0.468083	4.260225	1.835599
Br	3.365868	4.007054	4.109910
Br	2.925838	6.931155	1.759346
Br	2.954371	1.578598	1.363779
Br	2.898167	4.527174	-1.338054
Te	2.995220	4.244863	1.606380
Br	5.941803	4.461561	1.338054
Te	5.844750	4.743872	-1.606380
Br	8.371887	4.728510	-1.835599
Br	5.474102	4.981681	-4.109910
Br	5.914132	2.057580	-1.759346
Br	5.885599	7.410137	-1.363779
Br	3.064400	7.947209	4.708048
Br	3.268098	8.898847	6.827893
Br	9.377083	4.260225	1.835599
Br	12.274868	4.007054	4.109910
Br	11.834838	6.931155	1.759346
Br	11.863371	1.578598	1.363779
Br	11.807167	4.527174	-1.338054
Te	11.904220	4.244863	1.606380

Br	14.850803	4.461561	1.338054
Te	14.753750	4.743872	-1.606380
Br	17.280887	4.728510	-1.835599
Br	14.383102	4.981681	-4.109910
Br	14.823132	2.057580	-1.759346
Br	14.794599	7.410137	-1.363779
Br	-1.970360	3.128811	13.371539
Br	0.927425	2.875640	15.645850
Br	0.487395	5.799742	13.295287
Br	0.515929	0.447184	12.899719
Br	0.459724	3.395760	10.197887
Te	0.556777	3.113449	13.142320
Br	3.503360	3.330148	12.873994
Te	3.406307	3.612458	9.929561
Br	5.933445	3.597096	9.700342
Br	3.035660	3.850267	7.426031
Br	3.475690	0.926166	9.776594
Br	3.447156	6.278723	10.172162
Br	-2.039390	12.117546	13.371539
Br	0.858396	11.864375	15.645850
Br	0.418366	14.788476	13.295287
Br	0.446899	9.435919	12.899719
Br	0.390695	12.384495	10.197887
Te	0.487748	12.102184	13.142320
Br	3.434331	12.318883	12.873994
Te	3.337278	12.601193	9.929561
Br	5.864415	12.585831	9.700342
Br	2.966630	12.839002	7.426031
Br	3.406660	9.914901	9.776594
Br	3.378126	15.267458	10.172162
7			
Te	2.893165	4.101494	1.541144
Cl	0.543683	4.125166	1.708217
Cl	3.149113	3.892852	3.883857
Cl	2.795500	6.596837	1.728471
Cl	2.800174	1.591865	1.363216
Cl	2.855047	4.392153	-1.270448
Cl	5.749490	4.392588	1.270448
Te	5.711371	4.683247	-1.541144
Cl	8.060853	4.659575	-1.708217
Cl	5.455424	4.891889	-3.883857
Cl	5.809037	2.187904	-1.728471
Cl	5.804363	7.192876	-1.363216
Br	2.858621	7.669311	4.565912
Br	3.023820	8.684931	6.624501
Te	0.171070	11.670994	12.731557
Cl	-2.178412	11.694666	12.898630
Cl	0.427018	11.462352	15.074270
Cl	0.073405	14.166338	12.918884
Cl	0.078078	9.161366	12.553629
Cl	0.132952	11.961653	9.919965
Cl	3.027394	11.962089	12.460861
Te	2.989276	12.252747	9.649269
Cl	5.338758	12.229075	9.482197
Cl	2.733329	12.461389	7.306556
Cl	3.086942	9.757404	9.461942
Cl	3.082268	14.762376	9.827197

Te	0.238533	2.886253	12.731557
Cl	-2.110948	2.909925	12.898630
Cl	0.494481	2.677611	15.074270
Cl	0.140868	5.381597	12.918884
Cl	0.145542	0.376625	12.553629
Cl	0.200415	3.176912	9.919965
Cl	3.094858	3.177348	12.460861
Te	3.056740	3.468006	9.649269
Cl	5.406221	3.444334	9.482197
Cl	2.800792	3.676648	7.306556
Cl	3.154405	0.972663	9.461942
Cl	3.149731	5.977635	9.827197

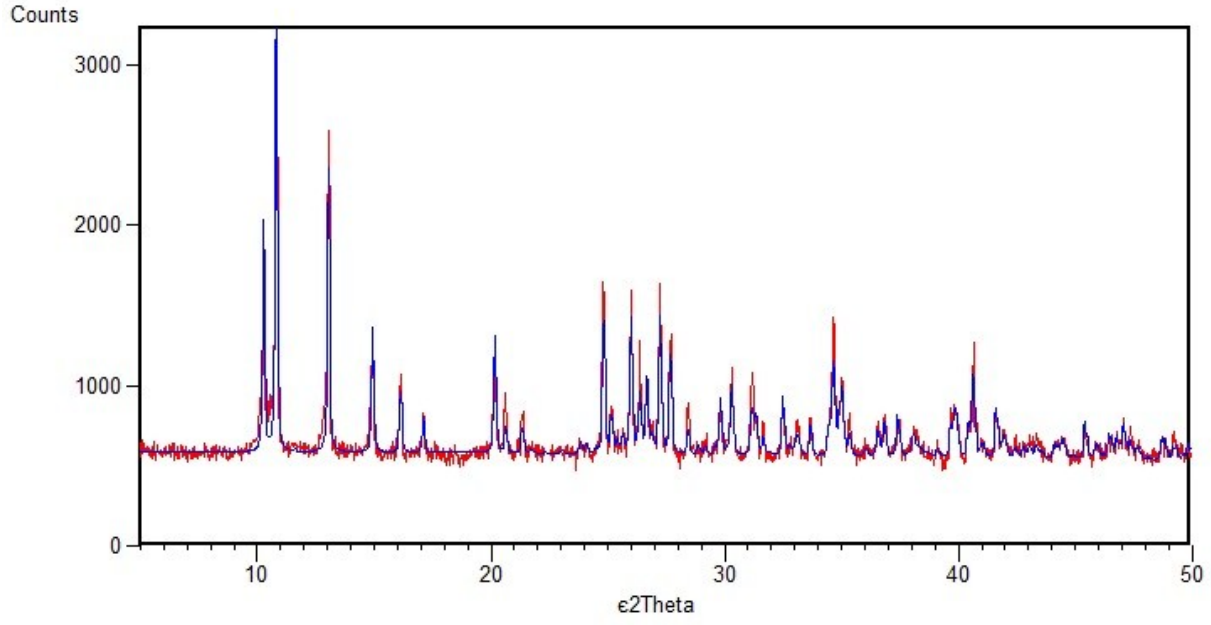

Figure 1S. PXRD analysis of the residue of **2** after the Br_2 loss (corresponds to **5**)

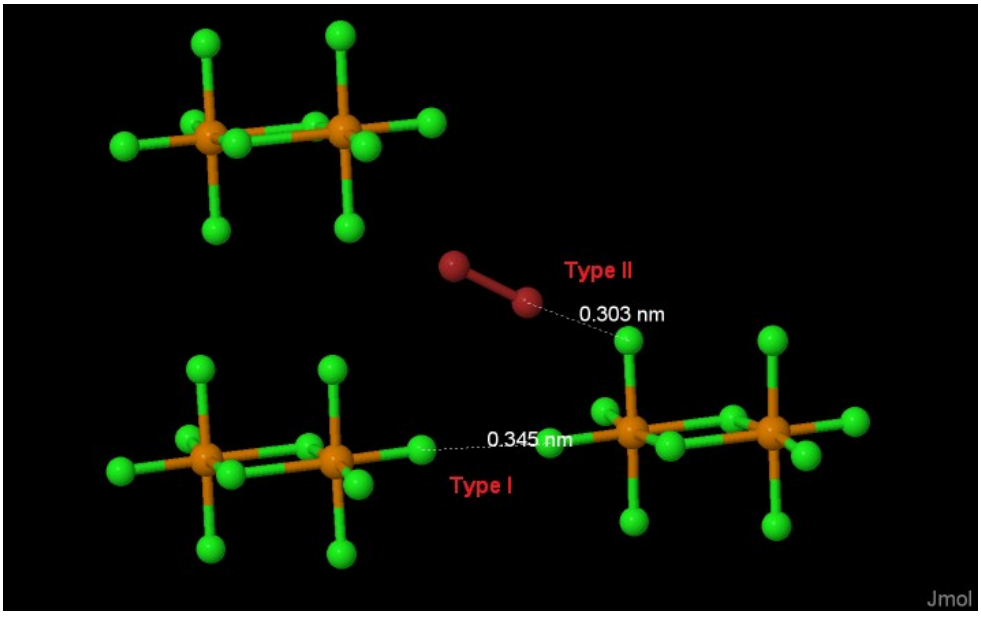

Figure 2S. Types of halogen-halogen contacts in **6**

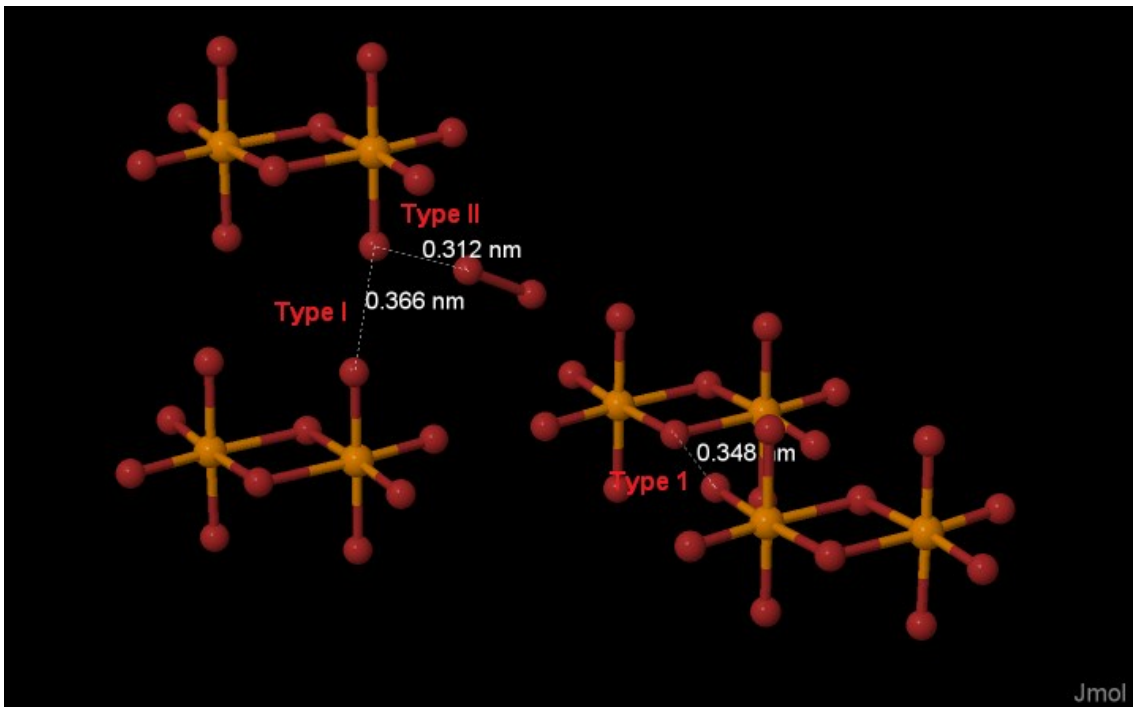

Figure 3S. Types of halogen-halogen contacts in **7**

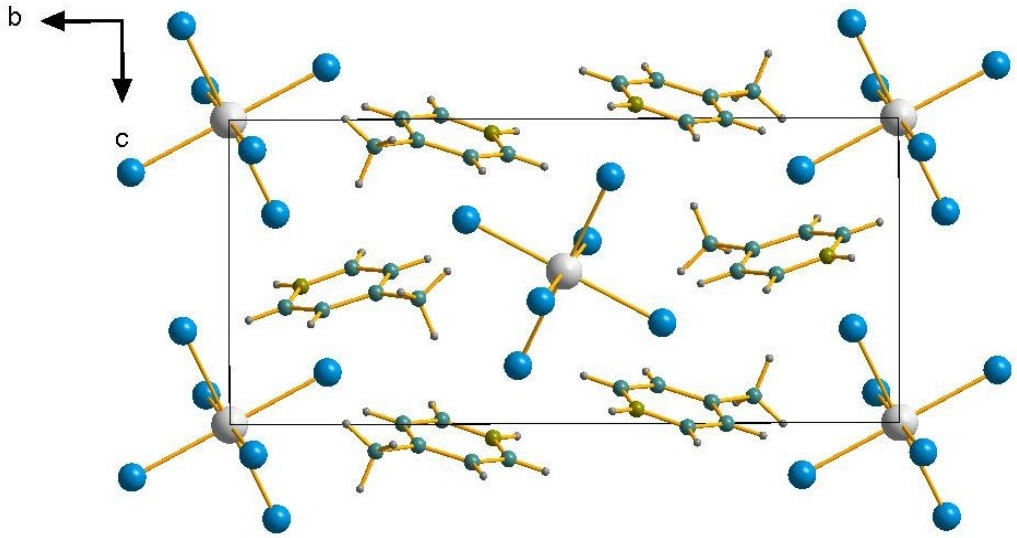

Figure 4S. Crystal packing in **5**